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 DETAILED DESCRIPTION

[Detailed description]

[0001]

[Field of the Invention] this invention relates to the art of the exhaust gas generated when chlorofluorocarbon is disassembled.

[0002]

[Prior art] Chlorofluorocarbon attracts attention as matter which an ozone layer is destroyed [matter] in recent years and worsens earth environment, and it is determined that chlorofluorocarbon (CFC) is abolished by A.D. 1996 and abolition and hydro chlorofluorocarbon (HCFC) are abolished by A.D. 2030 by the Montreal Protocol.

[0003] Then, the decomposition harmless-ized technique of chlorofluorocarbon is examined variously, and the research of a catalyst part solution method, a plasma part solution method, a combustion part solution method, a cement-kiln part solution method, an ultraviolet-rays part solution method, an electron ray part solution method, a super-criticality moisture solution method, a radiolysis method, a detonation part solution method, etc. is advanced until now. Also in which [these] technique, hydrogen fluoride or a fluorine and a hydrogen chloride, or chlorine occurs simultaneously as a decomposition product of chlorofluorocarbon, and since these have high detrimental nature as the issue is regulated by the Clean Air Act, it is required to process exhaust gas.

[0004] As a property of chlorofluorocarbon decomposition exhaust gas, the yield of exhaust gas other than the concurrence of hydrogen fluoride or a fluorine and a hydrogen chloride, or chlorine is sometimes large as compared with the throughput of chlorofluorocarbon. For example, the amounts of the hydrogen fluoride which in the case of the chlorofluorocarbon 113 (C2Cl3F3) which is one of most chlorofluorocarbon of the amount used is generated when 1kg of chlorofluorocarbon 113 is processed, and a hydrogen chloride are 0.32kg and 0.58kg, respectively, when these are further neutralized by the calcium hydroxide, the amount of the generated calcium fluoride and a calcium chloride is set to 0.62kg and 0.89kg, respectively, and the total quantity reaches by about 1.5 times the chlorofluorocarbon throughput.

[0005] In addition, it is shown by the following chemical formula when the example of the decomposition processing reaction of chlorofluorocarbon 113 is shown.

$C_2Cl_3F_3 + 3H_2O \rightarrow CO_2 + CO + 3HF + \dots$ a chemical formula is as follows when HF and HCl which were generated further 3 HCl are neutralized by the calcium hydroxide

It is shown by the following formula when neutralizing by the $2HF + \text{calcium}(\text{OH})_2 \rightarrow CaF_2 + 2H_2O + 2HCl + \text{calcium}(\text{OH})_2 \rightarrow CaCl_2 + 2H_2O$ sodium hydroxide.

A reaction is shown by the following formula when it decomposes under $HF + NaOH \rightarrow NaF + H_2O$ $HCl + NaOH \rightarrow NaCl + H_2O$ and an elevated temperature.

In processing by the sedimentation of $2C_2Cl_3F_3 + 4O_2 \rightarrow 4CO_2 + 3Cl_2 + 3F_2$ therefore the conventional art, for example, a scrubbing tower, and washing drainage etc., an offgas treatment facility will become very big as compared with a decomposition processing facility of chlorofluorocarbon, and will spoil greatly the economical efficiency of the whole chlorofluorocarbon decomposition processing facility.

[0006] On the other hand, although the saturation product of chlorofluorocarbon decomposition exhaust gas is the high matter of the usefulness like a calcium fluoride as mentioned above, since chlorofluorocarbon is processed independently in many cases, the amount of mixing of impurities other than a hydrogen chloride is very small, and it is effectively reusable if the chlorine compound which carries out saturation generation simultaneously is removed efficiently. However, since the amount of undissolved fluorine compounds, such as that a settling time needs to be secured and a generated calcium fluoride, is large, the sedimentation technique of the conventional drainage also about this will take a mass sedimentation facility, and the economical efficiency of the whole chlorofluorocarbon decomposition processing facility will be greatly spoiled by it. A lot of drainage which multiple times need to be washed in cold water in the fluorine compound which furthermore sedimented in order to obtain the fluorine compound of the high grade which is useful since soluble chlorine compounds (calcium chloride etc.) are intermingled, and is generated in that case will spoil the economical efficiency of a chlorofluorocarbon decomposition processing facility much more.

[0007] Moreover, when the fluorine concentration under drainage is regulated by 15 ppm or less and is carrying out self-imposed control severer than this by some local self-governing body further, as for fluorine inclusion drainage, for a certain reason, processing with advanced fluorine inclusion drainage is needed by Water Pollution Control Law. However, by technique, such as the conventional coagulation sedimentation, while drainage occurs in large quantities, a settling tank large-sized because of reservation of a settling time will be needed, a waste-water-treatment facility of large capacity [point / this] will be required, and

the economical efficiency of a chlorofluorocarbon decomposition processing facility will be spoiled.

[0008]

[Object of the Invention] Thus, when it applies to the exhaust gas which generates the art of the exhaust gas in the former when chlorofluorocarbon is disassembled, various problems are to process exhaust gas efficiently and carry out recovery reuse of the useful saturation product of exhaust gas efficiently, and there is no technique still completed even in the utilization phase. Then, the chlorofluorocarbon decomposition processing technique itself is not completed, but the development of the art of chlorofluorocarbon decomposition exhaust gas was desired also from this viewpoint.

[0009] It was made in order that this invention might solve such a conventional technical problem, and the place made into the purpose processes efficiently the exhaust gas generated when chlorofluorocarbon is disassembled, and it is in offering how a small-scale facility recovers a useful component.

[0010]

[A The means for solving a technical problem and an operation] The art of the 1st chlorofluorocarbon decomposition exhaust gas of this invention processes the exhaust gas which disassembled chlorofluorocarbon with a continuity and the circulation liquid which adds alkali quantitatively, and separates continuously the solid generated by saturation, and the dissolved salt from circulation liquid, and carries out the reuse of the circulation liquid.
 [0011] The art of the 2nd chlorofluorocarbon decomposition exhaust gas of this invention The exhaust gas which disassembled chlorofluorocarbon is processed with a continuity and the circulation liquid which adds alkali quantitatively. After mixing the solid which separates continuously the solid generated by saturation, and the dissolved salt from circulation liquid, and was separated with the circulation liquid from which both were removed and carrying out the lysis elimination of the impurities in a solid (fusibility salt etc.), a solid is separated again and the reuse of the circulation liquid is carried out.

[0012] The art of the 3rd chlorofluorocarbon cracked gas of this invention processes the exhaust gas which disassembled chlorofluorocarbon with a continuity and the circulation liquid which adds alkali quantitatively, and separates continuously the solid generated by saturation from circulation liquid, and carries out the reuse of the circulation liquid.

[0013] The art of the chlorofluorocarbon decomposition exhaust gas of the 1st and 2 makes the processing object the chlorofluorocarbon which contains chlorine and a fluorine as a component for chlorofluorocarbon (CFC), hydro chlorofluorocarbon (HCFC), etc. By the 1st technique, after separating a solid from circulation liquid by the 2nd technique to a solid being separated from circulation liquid, it washes in cold water by purified circulating water, an impurity is lessened, and purity is raised.

[0014] The art of the 3rd chlorofluorocarbon decomposition exhaust gas is aimed at a hydro fluorocarbon (HFC), i.e., the chlorofluorocarbon which there is no chlorine and contains a fluorine as a component, and does not have the process which separates the dissolved salt [in the 1st and the 2nd art therefore].

[0015] Next, the art of the 2nd chlorofluorocarbon decomposition exhaust gas containing the process of the art of the 1st and 3 is explained in full detail. The exhaust gas (it is named a harmful gas generically below.) containing the hydrogen fluoride generated by disassembly of chlorofluorocarbon or a fluorine and a hydrogen chloride, or chlorine is introduced into a scrubbing tower.

Although this scrubbing tower is selected according to a packed column, a spray tower, a cyclone scrubber, a venturi scrubber, the concentration of the harmful gas which it gets wet and 1 of ****, a crossflow contactor, a plate column, a bubbling tower, a jet scrubber, leakage ****, etc. or two or more generate, and temperature, all carry out the absorption saturation of the harmful-gas component in exhaust gas into a liquid by contact of exhaust gas and a liquid.

[0016] To the scrubbing tower, a continuity and the liquid which has alkali added quantitatively circulate, and a harmful gas is absorbed by this circulation liquid. As alkali, a calcium hydroxide, a sodium hydroxide, a calcium carbonate, a sodium carbonate, etc. can be used. It counteracts with a harmful gas in circulation liquid, and, as a result, such alkali forms a saturation product in the type of a fluorine compound and a chlorine compound.

[0017] After discharging these saturation products from a scrubbing tower, they are recoverable in the type of a solid as a useful object. In order to collect these from circulation liquid in the type of a high grade more, the purity of the useful object which can make the minimum the superfluous alkali component in circulation liquid, and collects the alkali of the equivalent required for saturation processing of the decomposition exhaust gas and the same amount for the addition of alkali as ***** a continuity and by supplying quantitatively according to the modality of chlorofluorocarbon for decomposition and a throughput can be improved. That is, since useful solids are collected where moisture is included, if the impurity is contained in this moisture, the purity of a recovery useful object will fall. Moreover, since useful objects are collected as a solid even if solids other than a useful object are in circulation liquid, the purity of a useful object falls. Since the purity of the useful object separated and collected simultaneously [with the useful solid which separated the alkali component of difficulty water solubility which is not case / the component / among these melted] like a calcium hydroxide and a calcium carbonate in the alkali added especially is spoiled or re-saturation operation of superfluous alkali is needed, this point is important in this invention.

[0018] Furthermore, especially in hydrogen fluoride or a fluorine, since the saturation product of difficulty solubility to generate forms a complicated hydrate near the neutralization-equivalent point and serves as colloid, trouble may be caused in the separation by dehydration of a solid performed by the lower-stream-of-a-river side. Therefore, the amount of the alkali to add needs to add to the luxus a little rather than the equivalent required for saturation of decomposition exhaust gas in the domain which does not spoil required purity, and to make circulation liquid into predetermined superfluous alkalinity as a recovery useful component. This predetermined superfluous alkalinity changes with alkali to use.

[0019] As an adjustment means of the addition of alkali, means to control the addition of alkali strictly, and also to add an acid continuously in circulation liquid in this invention can also be taken. Since the domain of PH to the aforementioned predetermined

superfluous alkalinity is known beforehand, superfluous alkalinity is controllable by carrying out feedback control of the amount of the acid which detects PH of circulation liquid and is continuously added based on it in a predetermined domain.

[0020] It is enabled to collect, without spoiling the purity of the calcium chloride which makes the saturation salt generated by using a hydrochloric acid in this invention the already contained calcium chloride, and collects them, since the calcium chloride is already contained in the circulation liquid which processes chlorofluorocarbon decomposition exhaust gas, although the acid to add can use a hydrochloric acid, a sulfuric acid, a nitric acid, etc.

[0021] It contains fluorine compounds, such as a calcium fluoride of difficulty solubility, and a sodium fluoride, and chlorine compounds, such as a soluble calcium chloride and a sodium chloride, using as a saturation product the circulation liquid which carried out the absorption saturation of the harmful gas by the scrubbing tower.

[0022] The precipitation solid of the parvus calcium fluoride of solubility or a sodium fluoride is first separated from the circulation liquid discharged from the scrubbing tower. As a separation means of a solid, although there are meanses, such as dehydration, vaporization concentration, and sedimentation, as a means to separate only a solid from circulation liquid quickly continuously, dehydration is the optimum. All can be used although meanses, such as a centrifugal hydroextraction, the filter press, a belt press, and vacuum dehydration, are in the dehydration technique.

[0023] Soluble salts, such as a calcium chloride, are succeedingly removed from the circulation liquid with which the solid was separated. As a means to remove the soluble salt which exists by the ionic state, although there are electrodialysis, reverse osmosis membrane processing, ion exchange, etc., as a means to separate only a soluble salt quickly, the electrodialyses is the optimum.

[0024] Since the sequence of carrying out elimination of the solid from the aforementioned circulation liquid and elimination of a soluble salt may shorten theoretically the life of the ion exchange membrane used by the electrodialyses when a high-concentration solid exists in circulation liquid by the electrodialyses in this invention for which a soluble salt is removed, although not specified, after it removes a solid first, it leads to removing a soluble salt carrying out this invention efficiently.

[0025] The solid separated from circulation liquid by dehydration can carry out recovery reuse as it is, when purity has reached the purity demanded from the mission used as a useful object. However, since the solid which the chlorine compound is intermingled by the ionic state as a soluble salt as mentioned above in the saturation product of chlorofluorocarbon decomposition exhaust gas in many cases, and can be obtained by dehydration usually contains 75 - 85% of moisture, impurities (soluble salt etc.) exist in this moisture, and it is insufficient of purity in many cases. To this, the content of a soluble salt can be aimed at the solid after dehydration with a few liquid, and enhancement in purity can be aimed at by washing in cold water and dehydrating again. However, introducing water from the exterior has the fault that a displacement increases.

[0026] In this invention, the purity of the solid separated, without the circulation liquid whose content of a soluble salt removed the soluble salt by the aforementioned electrodialyses and decreased performing this washing in cold water, and introducing water from the exterior (i.e., without it having increased the displacement) can be raised.

[0027] Although the soluble salt removed from circulation liquid by the electrodialyses is discharged from an electrodialyzer in the type of little concentration liquid, in the case of chlorofluorocarbon decomposition exhaust gas, this is the aqueous solutions, such as a calcium chloride of a high grade, and a sodium chloride. If concentration, xeransis, etc. still need to be operated and the cost which it takes is considered in order to make it the solid gestalt used in general industry, although this may be collected and reused since a calcium chloride and a sodium chloride are matter extensively used in general industry, not necessarily reusing is not a best policy economically. Therefore, by the case, these will be discharged as drainage.

[0028] In order that the drainage which generally contains a fluorine or a fluorine compound may satisfy severe regulation of Water Pollution Control Law, it needs many operations, such as coagulation sedimentation, and requires many facilities, such as a saturation facility relevant to it. In this invention, almost all fluorine compounds (CaF_2 , NaF , etc.) are separated for this drainage from circulation liquid by dehydration processing as a solid. Subsequently, an ion component is separated from circulation liquid by carrying out electrodialysis processing of the circulation liquid from which the solid was removed by dehydration processing. The detailed solid contents (CaF_2 , NaF , etc.) from which most salts (CaCl_2 , NaCl , etc.) melted at this time were not separated by dehydration processing while it dissociated from circulation liquid cannot penetrate ion exchange membrane, but remain in a circulation liquid side.

[0029] Only an ion component exists in the liquid separated by the electrodialyses. Although F^+ ion also exists in this, since the solubility of CaF_2 is 8 ppm, it can satisfy 15 ppm of effluent standards enough. Although solubility is larger than CaF_2 in NaF , it is only an ion component and F^+ ion can be lowered easily.

[0030]

[Example] Although an example is shown below, this invention is not limited to this.

(Example 1) this example is an example which processes the chlorofluorocarbon decomposition exhaust gas generated when a chlorofluorocarbon decomposition processor decomposes chlorofluorocarbon 11 (CCl_3F), and the equipment used here carries out decomposition processing of the chlorofluorocarbon with the processing speed of 50kg/h using a catalyst. A schematic diagram is shown in drawing 1.

[0031] After supplying the air of about 260Nm³/h to a heater (2) with a blower (1) and heating it as carrier gas of chlorofluorocarbon, chlorofluorocarbon is heated to the temperature of about 430 degrees C required for the decomposition by the catalyst by mixing the steam supplied through a flow control valve (3), and the chlorofluorocarbon supplied through a flow control valve (4). The concentration of chlorofluorocarbon is about three mol %.

[0032] what is used in order that a steam may supply hydrogen required for the decomposition by the catalyst of chlorofluorocarbon,

and oxygen -- it is -- the modality of chlorofluorocarbon, and a throughput -- responding -- 1.0- of the equivalent required for decomposition -- it supplies about 3.0 times The amount of supply of a steam is controlled to go into this domain.

[0033] Since temperature falls by mixture with chlorofluorocarbon, the air before mixture sets up the temperature of the air before mixture more highly from temperature required for the decomposition by the catalyst so that it may become more than the temperature that needs the temperature after the mixture with chlorofluorocarbon for the decomposition by the catalyst of chlorofluorocarbon. Moreover, the temperature of the air before mixture sets up the amount of supply of air and a steam so that the partial decomposition temperature of chlorofluorocarbon may not be exceeded, and it controls each amount of supply. Moreover, the output of a heater (2) is controlled for the temperature of air to become below the partial decomposition temperature of chlorofluorocarbon, and to become more than the temperature which needs the temperature after the mixture with chlorofluorocarbon for the decomposition by the catalyst of chlorofluorocarbon.

[0034] Since a steam generates the heating means of a heater (2) as products of combustion using the combustion burner which used the hydrocarbon propellant, it can fill up a steam required for a decomposition reaction.

[0035] The mixed gas of the air and the steam which were heated by the predetermined temperature requirement, and chlorofluorocarbon is introduced into a catalyst container (5), and is decomposed into a hydrogen chloride, hydrogen fluoride, a carbon dioxide, etc. by catalytic reaction. Decomposition-reaction heat is applied in heated temperature of about 430 degrees C, and the exhaust gas after decomposition is discharged at about 450 degrees C. Hydrogen fluoride and 7.3kg /of 39.8kg /of hydrogen chlorides are generatedh h, respectively.

[0036] Since corrosive is very high, the hot hydrogen chloride which occurs by decomposition, and hydrogen fluoride ease the corrosive environment of the equipment after it in this invention by cooling the cracked gas with corrosive [hot] in the interior of a catalyst container (5).

[0037] The domain with a severe corrosive environment is made into the minimum as a means of cooling, and the technique of carrying out the spray of the cracked gas immediately after considering as a means to stop pressure loss low, and coming out of a catalyst inside a catalyst container (5) with a liquid is selected. Although a stable liquid is used for this liquid chemically [water etc.], it can realize relief of much more corrosive environment by mixing alkali and neutralizing a halogen and a hydrogen halide partially.

[0038] Since it mixes into a catalyst, and the temperature of a catalyst may be reduced or the droplet of a spray may reduce the activity of a catalyst when carrying out the spray of the liquid inside [in which the catalyst was installed] a container, in this invention, it prevents that the droplet mixes in a catalyst by installing a baffle plate (6) between a catalyst and spray space.

[0039] moreover, in carrying out the spray of the liquid inside [in which the catalyst was installed] a container Since a new cauterization occurrence factor will be produced by carrying in hygroscopic moisture into this piping that the droplet of a spray shifts into piping which connects the scrubbing tower (8) by the side of the lower stream of a river with the container which installed the catalyst, and is originally drying, In this invention, by establishing the parvus separation room (7) of the rate of flow in the interior of a container in which the catalyst was installed, the droplet in the air is made to sediment and it prevents that the droplet shifts to down-stream piping.

[0040] With a catalyst container (5), cooling or after neutralizing partially, as for cracked gas, a hydrogen halide (HCl, HF) is completely removed by the scrubbing tower (8) of the following process. It adsorbs by the adsorption tower (9) with which non-decomposed chlorofluorocarbon filled up the active carbon which ***** rare ** installed in the lower-stream-of-a-river side of a scrubbing tower (8) in this invention into the cracked gas discharged from a scrubbing tower (8), and the chlorofluorocarbon from which it secedes after that at the time of regeneration of active carbon is returned to a catalyst container (5), and is processed again. Furthermore, in this invention, the chlorofluorocarbon which reproduced and desorbed is processed from an adsorption tower (9), without suspending decomposition processing of the chlorofluorocarbon which is a main decomposition processing object by reproducing the one remaining sequence and introducing into a catalyst on stream the chlorofluorocarbon which reproduced and desorbed, while using 2 sequence **** and one sequence for adsorption for this adsorption tower (9).

[0041] Circulation liquid is supplied to the scrubbing tower (8) by the flow rate of about 1.3m³/h using the circulation tub (10) and the circulating pump (11). This is introduced into a catalyst container (5), combines with the circulation liquid of about 1.2m³/h supplied to a catalyst container (5) as spray liquid, and circulates through the whole system as circulation liquid of about 2.5m³/h of the sums. It is necessary to set the amount of circulation liquid flows as the amount which ebullism and vaporization do not produce by the contact to about 450-degree C chlorofluorocarbon decomposition exhaust gas introduced into a scrubbing tower (8), and it serves as about 2.5m³/h in this example.

[0042] In the circulation tub (10), with the alkali hopper (12), 1 54.3kg [/] over% which is 53.8kg/h whose powdered calcium hydroxides are the required equivalent of a detrimental component is supplied to circulation liquidh, and circulation liquid is adjusted to it alkaline. Since this addition is strictly performed by the micro feeder, 1% is exceeded and it is not added superfluously.

[0043] For a parvus reason, in this example, the flow rate of a scrubbing tower (8) of circulation liquid is a spray tower, the harmful gas in chlorofluorocarbon decomposition exhaust gas is absorbed in circulation liquid in a spray, and it neutralizes with the calcium hydroxide in circulation liquid further, and hydrogen fluoride generates a calcium fluoride and a hydrogen chloride generates a calcium chloride. The material of a scrubbing tower (8) is carrying out Teflon coating of the internal surface of parietal bone for the corrosion prevention by the detrimental component introduced into a scrubbing tower (8).

[0044] Although the yields of these saturation products (a calcium fluoride, calcium chloride) are 14.2kg [h] /and 60.5kg/h, respectively Since the solubility of a calcium fluoride is as small as an about 15-20g/[m]3-solution near [concerned]

temperature and the solubility of a calcium chloride is as large as an about 400-500kg/m³-solution near [concerned] temperature, the inside of the circulation liquid of about 2.5m³/h -- the most exists and, as for a calcium chloride, in a calcium fluoride, the most exists as a soluble salt as an undissolved solid Moreover, the concentration in the inside of each liquid is about 0.6 % of the weight and about 2.3 % of the weight.

[0045] The circulation liquid which contains a calcium fluoride and a calcium chloride by the aforementioned amount and concentration is introduced into the back slurry supply tub (13) discharged from the scrubbing tower (8). In a slurry supply tub (13), circulation liquid is the cooling coil (14) installed in the interior of a slurry supply tub (13), and is cooled to the temperature suitable for dehydration of a back process, and the electrodiyses while it piles up about 30 minutes or more and a neutralization is completed in the meantime.

[0046] The circulation liquid with which saturation is completed and was cooled is introduced into the first dehydrator (16) by the first slurry feed pump (15) from a slurry supply tub (13). Circulation liquid is dehydrated by the first dehydrator (16), and, as for the calcium fluoride in circulation liquid, a water content is separated from circulation liquid with the gestalt of about 80% of a dehydration cake. Since about 2.3% of the weight of the calcium chloride is soluble in the moisture in a dehydration cake as aforementioned, the purity of the calcium fluoride at the time of drying this dehydration cake as it is is about 89%, when the calcium hydroxide which remains in circulation liquid while it has been unreacted is included, and is 95% or more widely demanded in general industries, such as a glass manufacture.

[0047] a part for the dehydration cake from which the circulation liquid with which the calcium fluoride was separated by the first dehydrator (16) was separated -- the flow rate is decreased, and it is discharged by the supernatant-liquid tub (17) from the first dehydrator (16) by the flow rate of about 2.4m³/h, and is further introduced into an electrodialyzer (19) with a waste fluid pump (18) In an electrodialyzer (19), a lysis component is removed from circulation liquid by the electrodiyses. Specifically, solubility of a calcium chloride is large, and since it exists in the type of ion, the most (about 90%) is removed. It is similarly removed about a melted part of a calcium fluoride.

[0048] From an electrodialyzer (19), the calcium chloride removed from circulation liquid is discharged by the flow rate of about 0.5m³/h as concentration liquid whose concentration is about 9 % of the weight. Since concentration is comparatively high, the concentration liquid of this calcium chloride is set and reused [collect and] to this example. It is also possible to condense further, to dry this and to collect calcium chlorides as a solid. Moreover, F⁻ ion concentration has the solubility of CaF₂ as small as about 8 ppm, and since a solid content does not exist, either, 15 ppm of effluent standards can be satisfied.

[0049] On the other hand, the calcium chloride which is a lysis component is separated, the concentration of a calcium chloride serves as the clear liquid purified with about 0.2 % of the weight which is about 1 before electrodiagnosis processing/10, and the circulation liquid which passed the electrodialyzer (19) is introduced into a rinse tub (21) with a clear liquid pump (20) by the flow rate of about 1.8m³/h. The calcium-fluoride dehydration cake separated into the rinse tub (21) from circulation liquid from the first dehydrator (16) is also introduced, and clear liquid and a dehydration cake are mixed inside a rinse tub (21). The calcium chloride of about 2.3 % of the weight of the concentration in a dehydration cake is diluted with clear liquid of about 0.2 % of the weight of concentration, and reduces the concentration to about 0.3 percentage by weight.

[0050] The interflow field of a calcium-fluoride dehydration cake and clear liquid is introduced into the second dehydrator (23) by the second slurry feed pump (22) from a rinse tub (21) as circulation liquid. Circulation liquid is again dehydrated in the second dehydrator (23), and, as for fluoride *****, a water content is separated from circulation liquid as about 80% of a dehydration cake. Since circulation liquid is reduced to about 0.3% of the weight in the calcium chloride concentration in the rinse tub (21), the calcium chloride in a dehydration cake will also decrease and the purity of the calcium fluoride at the time of drying this will fully exceed 97% and 95% of required purity by the case where the aforementioned calcium hydroxide is included.

[0051] The circulation liquid with which the calcium fluoride was separated by the second dehydrator (23) uses both calcium fluoride and calcium chloride as the clear liquid by which separation elimination was carried out, is discharged by the circulation tub (10) by the flow rate of about 1.8m³/h, has alkali again added by the alkali hopper (12), and is reused as circulation liquid.

[0052] in addition, the flow rate of the circulation liquid which the flow rate of the circulation liquid introduced into a scrubbing tower (8) from a circulation tub (10) is about 2.5m³/h in this example, and is introduced into a circulation tub (10) from the second dehydrator (25) -- about 1.8m³/h and circulation liquid -- about 0.7m³/h per circulation -- in order to reduce the flow rate, an insufficiency will be filled up in the suitable part on a circulation tub and other circulation lines

[0053] (Example 2) this example is an example which processes the chlorofluorocarbon decomposition exhaust gas generated when the chlorofluorocarbon decomposition processor which carries out decomposition processing of the chlorofluorocarbon with the processing speed of 50kg/h using a catalyst decomposes chlorofluorocarbon 12 (CCl₂F₂). A schematic diagram is shown in drawing 2.

[0054] Chlorofluorocarbon is introduced into a catalyst column (5) by back one mol % of the concentration mixed with the heated air and the steam. In a catalyst column, it hydrolyzes and hydrogen fluoride and a hydrogen chloride generate 16.5kg /of 30.2kg /of chlorofluorocarbon h as a harmful gas, respectively.

[0055] the air of about 800Nm³/h these [whose] are carrier gas, and decomposition -- secondary -- it is introduced into a scrubbing tower (8) with the little steam which is degree product, a carbon dioxide, a carbon monoxide, etc. The temperature of chlorofluorocarbon decomposition exhaust gas is about 440 degrees C, in order to apply the heat of decomposition of chlorofluorocarbon to heating temperature.

[0056] Circulation liquid is supplied to the scrubbing tower (8) by the flow rate of about 6.0m³/h using the circulation tub (10) and the circulating pump (11).

[0057] With the alkali hopper (12), 1 61.7kg [/] over% (0.6kg/h)) which is 61.1kg/h whose powdered calcium hydroxides are the saturation required equivalent of cracked gas is supplied, and circulation liquid is adjusted [in / the circulation tub (11) / in circulation liquid] alkaline. At this example, in order for a cheap rotary feeder to perform this addition, strict superfluous 1% addition is difficult, for this reason, an addition is considered as 1% or more of a superfluous setup, and a back process (24, 25) realizes the strict superfluous status 1% by PH adjustment by the acid.

[0058] Since the flow rate of circulation liquid is large in this example, a scrubbing tower (8) is a packed column formula, the harmful gas in chlorofluorocarbon decomposition exhaust gas is absorbed in circulation liquid in a filler, and it neutralizes with the calcium hydroxide in circulation liquid further, and hydrogen fluoride generates a calcium fluoride and a hydrogen chloride generates a calcium chloride. The material of a filler is using plastic material for the corrosion prevention by the detrimental component introduced into a scrubbing tower (8). The material of a scrubbing tower (8) is the same as that of an example 1.

[0059] the yield of these saturation products (a calcium fluoride, calcium chloride) -- respectively -- 32.2kg [h] / and 45.9kg/h -- it is -- the inside of the circulation liquid of about 6.0m³/h -- the most exists and, as for a calcium chloride, in a calcium fluoride, the most exists as a soluble salt (ion) as a solid. Moreover, the concentration in the inside of each liquid is about 0.5 % of the weight and about 0.7 % of the weight.

[0060] The circulation liquid which contains a calcium fluoride and a calcium chloride by the aforementioned amount and concentration is introduced into the back slurry supply tub (13) discharged from the scrubbing tower (8). In a slurry supply tub (13), circulation liquid is cooled to the temperature which was suitable for dehydration and the electrodialyses by the cooling coil (14) installed in the interior of a slurry supply tub (13) while it piles up about 30 minutes or more and a neutralization is completed in the meantime.

[0061] Although the circulation liquid with which saturation is completed and was cooled is introduced into the first dehydrator (16) by the first slurry feed pump (15) from a slurry supply tub (13), since alkali is superfluously added as aforementioned, by this example, the calcium hydroxide remains superfluously. Therefore, when calcium fluorides are collected as it is, a calcium hydroxide will mix in the collected calcium fluoride, and the purity of the collected calcium fluoride will be spoiled. In this example, the degree of overalkali is adjusted to 1% by adding a hydrochloric acid through the flow control valve (25) which detected PH of circulation liquid with PH meter (24) at the slurry supply tub (13) outlet, and controlled the opening by feedback control for **.

[0062] Circulation liquid is dehydrated for the circulation liquid which had alkalinity adjusted by the first dehydrator (16), and, as for the calcium fluoride in circulation liquid, a water content is separated from circulation liquid with the gestalt of about 80% of a dehydration cake. 95% or more which is about 95% including the calcium hydroxide which adds to 0.6 overkg/h in order that the purity of a calcium fluoride may perform dehydration and an electrodialyses efficiently, even if it dries this dehydration cake as it is, although about 0.7% of the weight of the calcium chloride is melting as the above [moisture / in a dehydration cake], and remains in circulation liquid while it has been unreacted, and is widely demanded in general industries, such as a glass manufacture, is satisfied. Therefore, in this example, washing-in-cold-water operation is unnecessary.

[0063] a part for the dehydration cake from which the circulation liquid with which the calcium fluoride was separated by the first dehydrator (16) was separated -- the flow rate is decreased, and it is discharged by the supernatant-liquid tub (17) from the first dehydrator (16) by the flow rate of about 5.8m³/h, and is further introduced into an electrodialyzer (19) with a waste fluid pump (18). In an electrodialyzer (19), a calcium chloride is removed from circulation liquid by the electrodialyses.

[0064] From an electrodialyzer (19), the calcium chloride removed from circulation liquid is discharged by the drainage tub (27) by the flow rate of about 1.0m³/h with a concentration liquid pump (26) as concentration liquid whose concentration is about 3 % of the weight. Since concentration is comparatively low, the concentration liquid of this calcium chloride is discharged as drainage by this example. In case of drainage, by the ion exchange membrane of an electrodialyzer (19), the calcium fluoride of the shape of a detailed solid is removed, the fluorine concentration under drainage has the solubility of the calcium fluoride melted further fully smaller than the regulation value of Water Pollution Control Law, and it does not need special fluorine elimination operation from 8 ppm and a small thing.

[0065] The calcium chloride which is a lysis component is separated, and calcium chloride concentration serves as the clear liquid purified with about 0.1 % of the weight which is about 1 before electrodialysis processing/10, and the circulation liquid which passed the electrodialyzer (19) on the other hand is introduced into a circulation tub (10) with a clear liquid pump (20) by the flow rate of about 4.8m³/h, has alkali again added by the alkali hopper (11), and is reused as circulation liquid.

[0066] (Example 3) this example is an example which processes the chlorofluorocarbon decomposition exhaust gas generated when the chlorofluorocarbon decomposition processor which carries out decomposition processing of the chlorofluorocarbon HFC with the processing speed of 50kg/h using a catalyst decomposes chlorofluorocarbon 134a. Since HFC does not contain chlorine, although there are no worries about an ozone crack, since there is the warming effect, it is detrimental from global-warming prevention, and there is the need for harmless-izing. A decomposition formula serves as $2CF_3CH_2F + 2H_2O + 3O_2 \rightarrow 8HF + 4CO_2$.

[0067] A schematic diagram is shown in drawing 3. After supplying the air of about 260Nm³/h to a heater (2) with a blower (1) and heating it as carrier gas of chlorofluorocarbon, chlorofluorocarbon is heated to the temperature of about 430 degrees C required for the decomposition by the catalyst by mixing the steam supplied through a flow control valve (3), and the chlorofluorocarbon supplied through a flow control valve (4). The concentration of chlorofluorocarbon is about three mol %.

[0068] what is used in order that a steam may supply hydrogen required for the decomposition by the catalyst of chlorofluorocarbon, and oxygen -- it is -- the modality of chlorofluorocarbon, and a throughput -- responding -- 1.0- of the equivalent required for decomposition -- it supplies about 3.0 times. The amount of supply of a steam is controlled to go into this domain.

[0069] Since temperature falls by mixture with chlorofluorocarbon, the air before mixture sets up the temperature of the air before mixture more highly from temperature required for the decomposition by the catalyst so that it may become more than the temperature that needs the temperature after the mixture with chlorofluorocarbon for the decomposition by the catalyst of chlorofluorocarbon. Moreover, the temperature of the air before mixture sets up the amount of supply of air and a steam so that the partial decomposition temperature of chlorofluorocarbon may not be exceeded, and it controls each amount of supply. Moreover, the output of a heater (2) is controlled for the temperature of air to become below the partial decomposition temperature of chlorofluorocarbon, and to become more than the temperature which needs the temperature after the mixture with chlorofluorocarbon for the decomposition by the catalyst of chlorofluorocarbon.

[0070] Since a steam generates the heating means of a heater (2) as products of combustion using the combustion burner which used the hydrocarbon propellant, it can fill up a steam required for a decomposition reaction. Moreover, the formula which heats indirectly the air which is carrier gas by combustion gas as a heat exchanger formula may be used. In this case, it is convenient, when maintaining a catalyst performance for a long period of time, since combustion gas etc. does not mix.

[0071] The mixed gas of the air and the steam which were heated by the predetermined temperature requirement, and chlorofluorocarbon is introduced into a catalyst container (5), and is decomposed into hydrogen fluoride, a carbon dioxide, etc. by catalytic reaction. Decomposition-reaction heat is applied in heated temperature of about 430 degrees C, and the exhaust gas after decomposition is discharged at about 450 degrees C. 39.1kg /of hydrogen fluoride is generatedh.

[0072] Since corrosive is very high, the hot hydrogen fluoride generated by decomposition eases the corrosive environment of the equipment after it in this invention by cooling the cracked gas with corrosive [hot] in the interior of a catalyst container (5).

[0073] The domain with a severe corrosive environment is made into the minimum as a means of cooling, and the technique of carrying out the spray of the cracked gas immediately after considering as a means to stop pressure loss low, and coming out of a catalyst inside a catalyst container (5) with a liquid is selected. Although a stable liquid is used for this liquid chemically [water etc.], it can realize relief of much more corrosive environment by mixing alkali and neutralizing hydrogen fluoride partially.

[0074] Since it mixes into a catalyst, and the temperature of a catalyst may be reduced or the droplet of a spray may reduce the activity of a catalyst when carrying out the spray of the liquid inside [in which the catalyst was installed] a container, in this invention, it prevents that the droplet mixes in a catalyst by installing a baffle plate (6) between a catalyst and spray space.

[0075] With a catalyst container (5), cooling or after neutralizing partially, as for exhaust gas, a hydrogen halide (hydrogen fluoride) is completely removed by the scrubbing tower (8) of the following process. To the cracked gas discharged from a scrubbing tower (8), what non-decomposed chlorofluorocarbon adsorbed by the adsorption tower (9) into which ***** rare ** filled up with this invention the active carbon installed in the lower-stream-of-a-river side of a scrubbing tower (8), and was reproduced is processed again. The decomposition luminous efficacy as a processing facility can be improved by this, and the amount of exudation non-decomposed chlorofluorocarbon can be reduced to 10 by about 1/. This effect twists non-decomposed chlorofluorocarbon to pass a catalyst bed again. In this case, non-decomposed chlorofluorocarbon is the lower stream of a river of a heater, and is supplied to the upstream of a catalyst. If this is supplied to the upstream of a heater, since it is over 700 degrees C which is the pyrolysis start temperature of chlorofluorocarbon partially in the heater, when non-decomposed chlorofluorocarbon is supplied to the upstream of a heater, it is to pyrolyze a part of chlorofluorocarbon and for a corrosive gas (HF) to occur. More nearly thereby than a catalyst bed, occurrence of the corrosive gas by the side of the upstream can be prevented, and enhancement in the endurance of a facility and use evasion of a high-class corrosion resisting material can be performed.

[0076] Furthermore, in this invention, the chlorofluorocarbon which reproduced and desorbed is processed from an adsorption tower (9), without suspending decomposition processing of the chlorofluorocarbon which is a main decomposition processing object by reproducing the one remaining sequence and introducing into a catalyst on stream the chlorofluorocarbon which reproduced and desorbed, while using 2 sequence **** and one sequence for adsorption for this adsorption tower (9).

[0077] Circulation liquid is supplied to the scrubbing tower (8) by the flow rate of about 1.3m3/h using the circulation tub (10) and the circulating pump (11). This is introduced into a catalyst container (5), combines with the circulation liquid of about 1.2m3/h supplied to a catalyst container (5) as spray liquid, and circulates through the whole system as circulation liquid of about 2.5m3/h of the sums. It is necessary to set the amount of circulation liquid flows as the amount which ebullism and vaporization do not produce by the contact to about 450-degree C chlorofluorocarbon decomposition exhaust gas introduced into a scrubbing tower (8), and it serves as about 2.5m3/h in this example.

[0078] In the circulation tub (10), with the alkali hopper (12), 1 73.0kg [/] over% which is 72.3kg/h whose powdered calcium hydroxides are the required equivalent of a detrimental component is supplied to circulation liquidh, and circulation liquid is adjusted to it alkaline. Since this addition is strictly performed by the micro feeder, it is not added by the luxus.

[0079] For a parvus reason, in this example, the flow rate of a scrubbing tower (8) of circulation liquid is a spray tower, the harmful gas in chlorofluorocarbon decomposition exhaust gas is absorbed in circulation liquid in a spray, it neutralizes with the calcium hydroxide in circulation liquid further, and hydrogen fluoride generates a calcium fluoride. The material of a scrubbing tower (8) is carrying out Teflon coating of the internal surface of parietal bone for the corrosion prevention by the detrimental component introduced into a scrubbing tower (8).

[0080] Although the yield of these saturation products is 14.0kg/h, the solubility of a calcium fluoride is as small as an about 15-20g/[m]3-solution near [concerned] temperature, and, as for a calcium fluoride, the most exists as a solid in the circulation liquid of about 2.5m3/h. Moreover, the concentration in the inside of liquid is about 0.6 % of the weight.

[0081] The circulation liquid which contains a calcium fluoride by the aforementioned amount and concentration is introduced into the back slurry supply tub (13) discharged from the scrubbing tower (8). In a slurry supply tub (13), circulation liquid is the

cooling coil (14) installed in the interior of a slurry supply tub (13), and is cooled to the temperature suitable for dehydration of a back process while it piles up about 30 minutes or more and a neutralization is completed in the meantime.

[0082] The circulation liquid with which saturation is completed and was cooled is introduced into the first dehydrator (16) by the first slurry feed pump (15) from a slurry supply tub (13). Circulation liquid is dehydrated by the first dehydrator (16), and, as for the calcium fluoride in circulation liquid, a water content is separated from circulation liquid with the gestalt of about 80% of a dehydration cake. Since there is no impurity in the moisture in a dehydration cake except [most] a calcium fluoride, even if the purity of the calcium fluoride at the time of drying this dehydration cake as it includes the calcium hydroxide which adds superfluously, and remains in circulation liquid while it has been unreacted, it is 95% or more widely demanded in general industries, such as a glass manufacture, and can collect the calcium fluorides with high purity.

[0083] a part for the dehydration cake from which the circulation liquid with which the calcium fluoride was separated by the first dehydrator (16) was separated -- the flow rate is decreased, and it is discharged by the supernatant-liquid tub (17) from the first dehydrator (16) by the flow rate of about 2.4m³/h, and is further returned to a circulation tub (10) with a waste fluid pump (18)

[0084] The circulation liquid with which the calcium fluoride was separated by the dehydrator (16) is discharged by the circulation tub (10) by the flow rate of about 2.4m³/h, has alkali again added by the alkali hopper (12), and is reused as circulation liquid.

[0085] in addition, the flow rate of the circulation liquid which the flow rate of the circulation liquid introduced into a scrubbing tower (8) from a circulation tub (10) is about 2.5m³/h in this example, and is introduced into a circulation tub (10) from a dehydrator (16) -- about 2.4m³/h and circulation liquid -- about 0.1m³/h per circulation -- in order to reduce the flow rate, an insufficiency will be filled up in the suitable part on a circulation tub and other circulation lines

[0086] (Example 4) this example is an example which processes the chlorofluorocarbon decomposition exhaust gas generated when the chlorofluorocarbon decomposition processor which carries out decomposition processing of the chlorofluorocarbon with the processing speed of 50kg/h using a catalyst decomposes chlorofluorocarbon 11 using the sodium-hydroxide aqueous solution. The schematic diagram is the same as that of drawing of an example 1.

[0087] After supplying the air of about 260Nm³/h to a heater (2) with a blower (1) and heating it as carrier gas of chlorofluorocarbon, chlorofluorocarbon is heated to the temperature of about 430 degrees C required for the decomposition by the catalyst by mixing the steam supplied through a flow control valve (3), and the chlorofluorocarbon supplied through a flow control valve (4). The concentration of chlorofluorocarbon is about three mol %.

[0088] what is used in order that a steam may supply hydrogen required for the decomposition by the catalyst of chlorofluorocarbon, and oxygen -- it is -- the modality of chlorofluorocarbon, and a throughput -- responding -- 1.0- of the equivalent required for decomposition -- it supplies about 3.0 times The amount of supply of a steam is controlled to go into this domain.

[0089] The mixed gas of the air and the steam which were heated by the predetermined temperature requirement, and chlorofluorocarbon is introduced into a catalyst container (5), and is decomposed into a hydrogen chloride, hydrogen fluoride, a carbon dioxide, etc. by catalytic reaction. Decomposition-reaction heat is applied in heated temperature of about 430 degrees C, and the exhaust gas after decomposition is discharged at about 450 degrees C. Hydrogen fluoride and 7.3kg /of 39.8kg /of hydrogen chlorides are generatedh h, respectively.

[0090] With a catalyst container (5), cooling or after neutralizing partially, as for exhaust gas, a hydrogen halide is completely removed by the scrubbing tower (8) of the following process.

[0091] Circulation liquid is supplied to the scrubbing tower (8) by the flow rate of about 1.3m³/h using the circulation tub (10) and the circulating pump (11). This is introduced into a catalyst container (5), combines with the circulation liquid of about 1.2m³/h supplied to a catalyst container (5) as spray liquid, and circulates through the whole system as circulation liquid of about 2.5m³/h of the sums. It is necessary to set the amount of circulation liquid flows as the amount which ebullism and vaporization do not produce by the contact to about 450-degree C chlorofluorocarbon decomposition exhaust gas introduced into a scrubbing tower (8), and it serves as about 2.5m³/h in this example.

[0092] In the circulation tub (10), with the alkali hopper (12), 1 64.6kg [/] over% which is 64.0kg/h whose powdered sodium hydroxides are the required equivalent of a detrimental component is supplied to circulation liquidh, and circulation liquid is adjusted to it alkaline. Since this addition is strictly performed by the micro feeder, it is not added by the luxus.

[0093] For a parvus reason, in this example, the flow rate of a scrubbing tower (8) of circulation liquid is a spray tower, the harmful gas in chlorofluorocarbon decomposition exhaust gas is absorbed in circulation liquid in a spray, and it neutralizes with the sodium hydroxide in circulation liquid further, and hydrogen fluoride generates a sodium fluoride and a hydrogen chloride generates a sodium chloride.

[0094] Although the yields of these saturation products (a sodium fluoride, sodium chloride) are 33.6kg [h] /and 46.8kg/h, respectively Since the solubility of a sodium fluoride is comparatively as small as an about 40kg/[m]3-solution near [concerned] temperature and the solubility of a sodium chloride is as large as an about 260kg/[m]3-solution near [concerned] temperature, the inside of the circulation liquid of about 2.5m³/h -- the most exists, and from eye the 3rd order, as an undissolved solid, since solubility of a sodium chloride is large, as for a sodium fluoride, the most exists as a soluble salt Moreover, the concentration in the inside of each liquid is about 1.3 % of the weight and about 1.8 % of the weight.

[0095] The circulation liquid which contains a sodium fluoride and a sodium chloride by the aforementioned amount and concentration is introduced into the back slurry supply tub (13) discharged from the scrubbing tower (8). In a slurry supply tub (13), circulation liquid is the cooling coil (14) installed in the interior of a slurry supply tub (13), and is cooled to the temperature suitable for dehydration of a back process, and the electrodialyses while it piles up about 30 minutes or more and a neutralization

is completed in the meantime.

[0096] The circulation liquid with which saturation is completed and was cooled is introduced into the first dehydrator (16) by the first slurry feed pump (15) from a slurry supply tub (13). Circulation liquid is dehydrated by the first dehydrator (16), and, as for the sodium fluoride in circulation liquid, a water content is separated from circulation liquid with the gestalt of about 80% of a dehydration cake. Since about 1.8% of the weight of the sodium chloride is soluble in the moisture in a dehydration cake as aforementioned, the purity of the sodium fluoride at the time of drying this dehydration cake as it is is about 90%, when the sodium hydroxide which adds to 0.6 overkg/h, and remains in circulation liquid while it has been unreacted is included, in order to perform dehydration and an electro dialyses efficiently, and is 95% or more widely demanded in general industries, such as a glass manufacture.

[0097] a part for the dehydration cake from which the circulation liquid with which the calcium fluoride was separated by the first dehydrator (16) was separated -- the flow rate is decreased, and it is discharged by the supernatant-liquid tub (17) from the first dehydrator (16) by the flow rate of about 2.4m³/h, and is further introduced into an electro dialyzer (19) with a waste fluid pump (18) In an electro dialyzer (19), the separation elimination of about 90% of the lysis component of a sodium chloride and a sodium fluoride is carried out by the electro dialyses from circulation liquid.

[0098] From an electro dialyzer (19), the sodium fluoride and sodium chloride which were removed from circulation liquid are discharged by the flow rate of about 0.5m³/h as concentration liquid. Since concentration is comparatively high, the concentration liquid of this sodium fluoride and a sodium chloride is set and reused [collect and] to this example. It is also possible to condense further, to dry this and to collect a sodium chloride and sodium fluorides as a solid.

[0099] On the other hand, the circulation liquid which passed the electro dialyzer (19) separates the solid content separated by dehydration processing, and the electro dialyses carries out the separation elimination of about 90% of a lysis component, and it is clear liquid. This circulation liquid that carried out the defecation is introduced into a rinse tub (21) with a clear liquid pump (20) by the flow rate of about 1.8m³/h. The sodium-fluoride dehydration cake separated into the rinse tub (21) from circulation liquid from the first dehydrator (16) is also introduced, and clear liquid and a dehydration cake are mixed inside a rinse tub (21). The sodium chloride of about 1.3 % of the weight of the concentration in a dehydration cake is diluted with clear liquid of about 0.1 % of the weight of concentration, and reduces the concentration to about 0.2 percentage by weight.

[0100] The interflow field of a sodium-fluoride dehydration cake and clear liquid is introduced into the second dehydrator (23) by the second slurry feed pump (22) from a rinse tub (21) as circulation liquid. Circulation liquid is again dehydrated in the second dehydrator (23), and, as for a sodium fluoride, a water content is separated from circulation liquid as about 80% of a dehydration cake. Since circulation liquid is reduced to about 0.2% of the weight in the sodium chloride concentration in the rinse tub (21), the sodium chloride in a dehydration cake can also decrease and the purity of the sodium fluoride at the time of drying this can obtain the high thing of the value added fully exceeding 95%.

[0101] The circulation liquid with which the sodium fluoride was separated by the second dehydrator (23) uses both sodium fluoride and sodium chloride as the clear liquid by which separation elimination was carried out, is discharged by the circulation tub (10) by the flow rate of about 1.8m³/h, has alkali again added by the alkali hopper (12), and is reused as circulation liquid.

[0102] in addition, the flow rate of the circulation liquid which the flow rate of the circulation liquid introduced into a scrubbing tower (8) from a circulation tub (10) is about 2.5m³/h in this example, and is introduced into a circulation tub (10) from the second dehydrator (25) -- about 1.8m³/h and circulation liquid -- about 0.7m³/h per circulation -- in order to reduce the flow rate, an insufficiency will be filled up in the suitable part on a circulation tub and other circulation lines

[0103]

[Effect of the invention] As explained above, this invention neutralizes chlorofluorocarbon decomposition exhaust gas with the circulation liquid of alkali addition quantitatively and continuously, saturation products are continuously removed and collected from circulation liquid, since it is the art of the chlorofluorocarbon decomposition exhaust gas which repeats and uses most circulation liquid, the decomposition exhaust gas of chlorofluorocarbon is processed efficiently, if still required in the fluoride salt solid of a useful component, chlorination salts can be collected efficiently, and it is [effect / in which that it is small-scale can carry out / **** /-izing of this invention

[Translation done.]

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DETAILED DESCRIPTION

[Detailed description]

[0001]

[The technical field to which invention belongs] this invention relates to recycling or the harmless-ized processor, and its art of the waste printed circuit board which occurs especially in connection with processing and which mainly has the processor of organic system detrimental exhaust gas about recycling or the harmless-ized processor, and its art of a waste printed circuit board.

[0002]

[Prior art] Electronic-intelligence devices, such as a personal computer and a word processor, have a very quick speed of a technical innovation, and the model change is performed per several months. For this reason, an user will replace these electronic-intelligence devices with the newest model in an average of five years, and, as for the replaced old thing, most serves as a disposal.

[0003] the printed circuit board which carried many electronic parts, such as LSI and a connector, in the interior of the mainframe of an electronic-intelligence device by soldered joint -- about 20 -- about [wt%] -- it contains When a landfill is carried out since the lead which is detrimental heavy metal, tin, antimony, the arsenic, etc. are contained while valuables, such as gold and copper, are contained in these printed circuit boards so much and shining, such detrimental heavy metal elutes in the earth, and the load to an environment is large.

[0004] From this, recycling of valuables or a detrimental object is separated, solder and electronic parts are separated from the eccrisis of the electronic-parts loading printed circuit board aiming at harmless-izing of the last eccrisis, or the waste printed circuit board processor and art which collect valuables, such as gold and copper, from a substrate mainframe further are examined. There is the technique or equipment shown for example, in the following (1) - (5) among the arts or equipments of the waste printed circuit board or waste plastic sheet already known.

[0005] (1) How to disassemble electronic parts from the printed circuit board which has the elimination process which applies melting or the heating process made to decompose, impulse force, etc. for the adhesives on which it is the technique of disassembling electronic parts from a printed circuit board, and electronic parts are pasted up, and removes the aforementioned parts from the aforementioned printed circuit board. Refer to the Japan patent official report of No. 2601225.

[0006] (2) The low-temperature melt recovery system which melting of the low-temperature melt which adhered to the printed circuit board by making a printed circuit board convey along a conveyance way, and injecting elevated-temperature gas to a substrate by the predetermined pressure on the way is carried out [recovery system], and makes it remove. Refer to publication-number 274461 [eight to] official report.

[0007] (3) Technique apply and pulverize the external force which carries out coarse grinding of the printed circuit board first, and contains compressive force and shearing force in the obtained coarse-grinding object, and a gravity separation and an electrostatic separation recover valuables from a printed circuit board further. Refer to publication-number 251154 [seven to] official report.

[0008] (4) It is the art of the printed circuit board scrap wood characterized by roasting printed circuit board scrap wood in the steam ambient atmosphere at the temperature below copper 400 degrees-C or more melting point, burning an exhaust gas with a combustion furnace, and emitting CO into the atmospheric air except for a detrimental component, such as oxidizing. Refer to publication-number 71521 [eight to] official report.

[0009] (5) The art of the cracked gas of the fire-resistant plastics characterized by carrying out wet recovery of the component which burns or pyrolyzes the plastics containing an antimony compound and a halogenated compound, is made to burn or pyrolyze the cracked gas which occurs in that case in 2nd order above 800 degrees C, carries out dry-type recovery of the component which makes an antimony oxide a subject after that, and makes a halogen a subject further as a flame retarder. Refer to the Japan patent official report of No. 2665192.

[0010]

[Object of the Invention] The principal components which constitute a printed circuit board mainframe are thermosetting resin, such as epoxy and a phenol, and the flame retarder which contained the bromine in this is added. For this reason, if a printed circuit board is heated, the exhaust gas of an organic system will be generated, and in it, many detrimental methyl bromides with which are the ozone-layer-depletion matter and carcinogenic are indicated to be also to the human body are contained. these organic system exhaust gas -- near 50 degree C -- it begins to generate from the degree of low temperature comparatively, and

increases abruptly at the temperature of 270 degrees C or more. Therefore, since temperature rises at 50 degrees C or more locally by friction when heating a printed circuit board at a heater etc., and external force is applied [not to mention] to a substrate and it deforms, cuts or crushes, the above-mentioned detrimental gas occurs. Therefore, in above processors and arts for a printed circuit board, the exhaust gas harmless-ized device is required.

[0011] However, with the technique or equipment of the above (1), (2), and (3), since it does not have the process or the device in which exhaust gas is processed, exhaust gas is emitted into the atmospheric air as it is. Although the organic gas which made the methyl bromide the start by combustion by this technique although it was emitting into the atmospheric air by the technique of (4) after having led exhaust gas to the combustion furnace and burning it is decomposed, the strong corrosive hydrogen bromide which this generates is emitted into the atmospheric air as it is, and causes acid rain. Although wet recovery of the component which burns or pyrolyzes exhaust gas at the elevated temperature of 800 degrees C or more, and makes a halogen a subject after that is carried out by the technique of (5), there is a problem that an energy cost is large, for an elevated temperature.

[0012] The purpose of this invention was not made in view of the above-mentioned trouble, and is to offer the waste printed circuit board processor which detrimental exhaust gas does not generate in process of recycling or harmless-ized processing, and its art.

[0013]

[The means for solving a technical problem] In the waste printed circuit board processor and its art of this invention, it is mainly characterized by the thing which occurs at the time of processing of heating of a substrate, deformation, a disconnection, or spallation and for which it has exhaust gas catalyst thermal decomposition equipment and an exhaust air scrubber in a component as an object for processing of organic system exhaust gas. By preparing an exhaust gas catalyst heating apparatus and an exhaust air scrubber, the detrimental exhaust gas generated in the above-mentioned processing of a waste printed circuit board is made harmless, and is not discharged out of equipment. For example, an exhaust gas catalyst heating apparatus decomposes a detrimental methyl bromide into a hydrogen bromide, a carbon dioxide, and water. In addition, ordinary hydrocarbons are disassembled into a carbon dioxide and water. Although a hydrogen bromide is the acid, it is neutralized by the exhaust air scrubber and it serves as a bromination salt and water. Bromination salts can be dried and collected.

[0014] Thus, exhaust gas is made harmless. And by using a catalyst heating apparatus, heating temperature can be held down to 800 degrees C or less, and can reduce an energy cost. And since it can decompose also by thin concentration, concentration adjustment of gas is free. It is that it is possible to make this, i.e., gas, mix air etc. and to carry out thin to the concentration below the explosion limit, and is desirable on safe. Since it is decomposition of an organic component as gas to mix, it is required for oxygen to contain, and air is desirable.

[0015] It is more effective if it considers as exhaust gas catalyst thermal decomposition equipment, the waste printed circuit board processor which has an exhaust air scrubber, and its art into the component of the waste printed circuit board processor which separates solder and electronic parts from a substrate by heating the eccentricity of the printed circuit board in which electronic parts were carried in this invention more than the melting temperature of solder, and applying external force, such as a pneumatic pressure by vibration, impact, the centrifugal force, a friction, or hot jet, to a substrate.

[0016] The catalyst for exhaust gas catalyst thermal decomposition equipment of this invention consists of one sort or two sorts or more of oxides chosen out of Si, aluminum, Ti, and Zr. As a modality of oxide, they are SiO₂, aluminum₂O₃, TiO₂, and ZrO₂, for example. Although there is a grade, it is not limited to these.

[0017] It is good to consider as the catalyst which added one sort or two sorts or more of metals further chosen out of Pt, Cu, nickel, and W to the above-mentioned oxide preferably. Pt, Cu, nickel, and W may be oxides.

[0018] The penetrant remover for exhaust air scrubbers of this invention is the water of alkali matter, such as a sodium hydroxide or a calcium hydroxide, or a solution to the inside of an alcoholic system organic solvent. Since the solubility of the bromination salt reacted and generated is low when an alcoholic system solvent is used, it precipitates, shortly after reacting. For this reason, compared with the case where recovery of a bromination salt is aqueous intermediation, it is easy. Moreover, since a carbon dioxide also serves as a salt simultaneously by alkali, exudation into the atmospheric air of a carbon dioxide can also be suppressed.

[0019] In this invention, you may form exhaust air gas-cooling-method equipment after catalyst thermal decomposition equipment. A cooling system can apply general heat exchangers, such as a coil type, shell, and a tube type.

[0020] Moreover, you may form the cyclone for water mist eliminators after an exhaust air scrubber.

[0021] Although catalyst heating temperature should just be within the limits of 250-800 degrees C in this invention, within the limits of 300-600 degrees C is desirable in fact.

[0022] Since the harmful gas generated in recycling or harmless-ized processing by considering as such a waste printed circuit board processor and its art is made harmless within equipment, it does not emit into the atmospheric air. For this reason, the low waste printed circuit board processor and its art of the safety which generates neither an ozone depleter nor an air pollution substance, high-reliability, and an energy cost can be offered.

[0023] In addition, the object of this invention is not limited to a waste printed circuit board, but can be applied to the recycling equipment of all the products using the resin with which the ** halogen flame retarder was added.

[0024]

[Gestalt of implementation of invention] Hereafter, although this invention is explained based on an example, this invention is not limited to these.

[0025] Drawing 1 is a waste printed circuit board treatment-process view which is one example of this invention.

[0026] The process shown in drawing 1 consists of the waste printed circuit board 1, the processor 2, the processed waste printed circuit board 3, exhaust gas catalyst thermal decomposition equipment 4, an exhaust air scrubber 5, and the exhaust gas 6 made harmless.

[0027] In drawing 1, the waste printed circuit board 1 is processed by the processor 2, and turns into the processed waste printed circuit board 3. It is the equipment which carries out processing of such combination, such as heating, deformation, a disconnection, and spallation, to the waste printed circuit board 1 in a processor 2 here, for example, the equipment which heats a substrate, is made to gasify a resin and carries out malacia processing or the equipment which disconnects electronic parts by the cutter etc. and is separated from a substrate, and a substrate are crushed as it is, and the ****-ized equipment is mentioned. From the waste printed circuit board 1, it goes up on the whole [temperature] or locally by heating or friction in this process, and the gas of the hydrocarbon system containing the detrimental methyl bromide occurs.

[0028] It is decomposed by the exhaust gas catalyst thermal decomposition equipment 4, and this hydrocarbon system gas turns into inorganic gas. The equipment constituted as catalyst thermal decomposition equipment 4 at the coil which filled up the interior with the catalyst, for example, and electric heating kiln can be considered. The great portion of inorganic gas is a carbon dioxide and a steam. It decomposes and a methyl bromide serves as a hydrogen bromide, a carbon dioxide, and a steam. It is washed or neutralized and these inorganic gas is made harmless by the exhaust air scrubber 5.

[0029] For example, when the caustic-alkali-of-sodium aqueous solution is used for this penetrant remover, it is absorbed, when a hydrogen bromide serves as a sodium bromide and a carbon dioxide serves as a salt as a sodium carbonate, respectively. As an exhaust air scrubber, there are a formula which injects a spray, for example, a formula using a packed column, a formula which carries out the direct bubbling of the gas into a penetrant remover. Exhaust gas harmless-changes according to the above process, and it is emitted as exhaust gas 6 made harmless.

[0030] Drawing 2 is a waste printed circuit board treatment-process view which is one example of this invention.

[0031] The process shown in drawing 2 consists of the waste printed circuit board 1, heating-apparatus 2a, external force additional-equipment 2b, substrate 3a that were separated, electronic-parts 3b which were separated, solder separated 3c, exhaust gas catalyst thermal decomposition equipment 4, an exhaust air scrubber 5, and the exhaust gas 6 made harmless.

[0032] In drawing 2, the waste printed circuit board 1 is heated by heating-apparatus 2a more than at the melting temperature of solder, and melting of the solder is carried out. External force is added by external force additional-equipment 2b, with the melting status maintained, and the waste printed circuit board 1 is divided into substrate 3a separated, electronic-parts 3b which were separated, and about three separated kinds of solder 3c. Here, heating-apparatus 2a and external force additional-equipment 2b do not need to be another fields, and may be one. For example, external force additional-equipment 2b may be in the interior of heating-apparatus 2a, and heating-apparatus 2a may be in the interior of external force additional-equipment 2b.

[0033] There is equipment which adds vibration, impact, a centrifugal force, a friction, or the pneumatic pressure by hot jet to the waste printed circuit board 1 as external force additional-equipment 2b, for example. This heating-apparatus 2a and the exhaust gas generated in external force additional-equipment 2b harmless-change by the same process 4 as drawing 1, i.e., an exhaust gas catalyst heating apparatus, and the exhaust air scrubber 5, and is emitted as exhaust gas 6 made harmless.

[0034] Drawing 3 is a waste printed circuit board treatment-process view which is one example of this invention.

[0035] The process shown in drawing 3 consists of the waste printed circuit board 1, the processor 2, the processed waste printed circuit board 3, the exhaust gas catalyst thermal decomposition equipment 4, the exhaust air gas-cooling-method equipment 7, an exhaust air scrubber 5, a cyclone 8, and the exhaust gas 6 made harmless.

[0036] In drawing 3, exhaust gas is once cooled with the exhaust air gas-cooling-method equipment 7 after decomposition by the exhaust gas catalyst thermal decomposition equipment 4. By cooling here, the temperature rise of the penetrant remover of the exhaust air scrubber 5 and vaporization are prevented. Exhaust gas is introduced into the cyclone after transit 8 in the exhaust air scrubber 5. Here, the decrement in a penetrant remover can be prevented by removing the moisture in exhaust gas and returning to the exhaust air scrubber 5. Thus, it dries and the exhaust gas 6 made harmless is emitted. In addition, removing moisture does not limit to a cyclone and it is not cared about at all by other technique, such as a demister. Moreover, only for either, the exhaust air gas-cooling-method equipment 7 and the cyclone 8 are.

[0037] Hereafter, the example of an experiment is explained.

[0038] (Example 1 of an experiment)

[0039]

[Table 1]

表 1

	排気ガス中の各成分の濃度 (vol ppm)				
	CH ₃ Br	C ₂ H ₅ Br	炭化水素類	CO ₂	HBr
ガス分解前	36.8	3.5	44.4	180	270
ガス分解後	0.01以下	0.01以下	0.01以下	345	336
洗浄後	0.01以下	0.01以下	0.01以下	75.1	0.1以下

[0040] In the atmospheric air, the waste printed circuit board was applied for 10 minutes, and the jaw crusher ground it. The ambient-atmosphere air under trituration is attracted by 3/min 1m, and it is TiO_2 . WO_3 SiO_2 It decomposed at 500 degrees C using the included oxide catalyst of $\text{Ti}:\text{W}:\text{Si}=7:2:1$. Space velocity was set to 10000/h. Spray washing of the gas after decomposition was carried out using NaOH aqueous solution of 1N. The main exhaust gas composition before and behind decomposition and after spray washing is shown in Table 1. The hydrocarbons which make a methyl bromide the start disappear after gas decomposition, and the mineralization is carried out. Moreover, after spray washing, the hydrogen bromide generated by gas decomposition disappears, and is neutralized. Moreover, a carbon dioxide also understands after spray washing concentration is falling and absorbed by NaOH.

[0041] (Example 2 of an experiment)

[0042]

[Table 2]

表 2

	排気ガス中の各成分の濃度 (vol ppm)				
	CH_3Br	$\text{C}_2\text{H}_5\text{Br}$	炭化水素類	CO_2	HBr
ガス分解前	138	5.7	176	405	419
ガス分解後	0.01以下	0.01以下	0.01以下	1060	523
洗浄後	0.01以下	0.01以下	0.01以下	228	0.1以下

[0043] Next, a waste printed circuit board is put into an electric furnace, and it is 120l/min about air. It heated for 20 minutes at 150 degrees C, introducing into an electric furnace at a rate. It is Pt to aluminum 2O_3 about the issue air from the electric furnace under heating 0.5wt% It decomposed at 700 degrees C using the included catalyst. Space velocity was set to 50000/h. It is calcium $(\text{OH})_2$ of 1N about the gas after decomposition. Spray washing was carried out using the aqueous solution. The main exhaust gas composition before and behind decomposition and after spray washing is shown in Table 2. Like the example 1 of an experiment, the mineralization of the hydrocarbons which make a methyl bromide the start is carried out by gas decomposition, and the hydrogen bromide is also neutralized. Moreover, concentration falls and a carbon dioxide is also calcium $(\text{OH})_2$. It was absorbed.

[0044] (Example 3 of an experiment)

[0045]

[Table 3]

表 3

	排気ガス中の各成分の濃度 (vol ppm)				
	CH_3Br	$\text{C}_2\text{H}_5\text{Br}$	炭化水素類	CO_2	HBr
ガス分解前	207	8.0	355	1132	788
ガス分解後	0.01以下	0.01以下	0.01以下	1388	1019
洗浄後	0.01以下	0.01以下	0.01以下	388	0.1以下

[0046] Next, a waste printed circuit board is put into an electric furnace, and it is 120l/min about air. The temperature up was carried out until it became 230 degrees C, introducing into an electric furnace at a rate. Vibration was added to the substrate for 5 minutes with excitation equipment after 230 degree-C attainment. It is issue air from the electric furnace at this time ZrO_2 It decomposed at 500 degrees C using the oxide catalyst of $\text{Zr}:\text{Cu}=9:1$ containing CuO . Space velocity was set to 5000/h. Bubbling washing of the gas after decomposition was carried out using KOH aqueous solution of 1N. The main exhaust gas composition before and behind decomposition and after spray washing is shown in Table 3. Like the examples 1 and 2 of an experiment, the mineralization of the hydrocarbons is carried out by gas decomposition, it disappears, and the hydrogen bromide is also neutralized. Moreover, concentration falls by KOH and the carbon dioxide was also absorbed.

[0047] (Example 4 of an experiment)

[0048]

[Table 4]

表 4

	排気ガス中の各成分の濃度 (vol ppm)				
	CH ₃ Br	C ₂ H ₅ Br	炭化水素類	CO ₂	HBr
ガス分解前	389	14.7	884	2025	1397
ガス分解後	0.01以下	0.01以下	0.01以下	2671	1998
洗浄後	0.01以下	0.01以下	0.01以下	794	0.1以下

[0049] Next, a waste printed circuit board is put into an electric furnace, and it is 120l./min about air. It is ordinary temperature to about 10 degrees C/min, introducing into an electric furnace at a rate. The temperature up was carried out until it became 320 degrees C by the programming rate. At this time, the issue air from the electric furnace in the temperature up from 270 degrees C to 320 degrees C was decomposed at 500 degrees C using NiO catalyst. Space velocity was set to 10000/h. The packed column washed the gas after decomposition using NaOH aqueous solution of 1N. The main exhaust gas composition before and behind decomposition and after packed column washing is shown in Table 4. Like the examples 1, 2, and 3 of an experiment, the mineralization of the hydrocarbons is carried out by gas decomposition, it disappears, and the hydrogen bromide is also neutralized. Moreover, concentration falls by NaOH and the carbon dioxide was also absorbed.

[0050] (Comparative experiments 1)

[0051]

[Table 5]

表 5

	排気ガス中の各成分の濃度 (vol ppm)				
	CH ₃ Br	C ₂ H ₅ Br	炭化水素類	CO ₂	HBr
ガス分解前	368	9.5	749	1857	1181
300℃ガス分解後	343	8.2	818	1914	1222
洗浄後	316	8.0	775	794	0.1以下
500℃ガス分解後	308	8.8	847	2005	1315
洗浄後	290	8.0	829	824	0.1以下
700℃ガス分解後	246	5.4	1105	2671	1998
洗浄後	221	4.9	1028	957	0.1以下

[0052] Next, it is ordinary temperature to about 10 degrees C/min, putting a waste printed circuit board into an electric furnace as a comparison, and introducing air into an electric furnace at a rate of 120l./min. The temperature up was carried out until it became 320 degrees C by the programming rate. At this time, the issue air from the electric furnace in the temperature up from 270 degrees C to 320 degrees C was decomposed using another electric furnace not using the catalyst at 300 degrees C, 500 degrees C, or 700 degrees C. The retention time at this time could be 3 seconds. The packed column washed the gas after decomposition using NaOH aqueous solution of 1N. The main exhaust gas composition before and behind decomposition and after packed column washing is shown in Table 5. In this case, at such temperature, it was hardly decomposed, therefore the hydrocarbons which made the methyl bromide the start were not absorbed by washing, either.

[0053]

[Effect of the invention] According to this invention, the waste printed circuit board processor which detrimental exhaust gas does not generate in process of recycling or harmless-ized processing, and its art can be offered as mentioned above.

[Translation done.]